

Zn in NZ mine drainages – controls on concentration

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Abstract

Zinc is one of the most abundant transition metals in mine drainages from coal mines and epithermal gold mines in New Zealand. Zinc is commonly conservative within mine drainage systems and remains in solution at concentrations that exceed guideline values for protection of aquatic ecosystems at pH<7. At operating mine sites, Zn is removed from mine drainages before discharge by active water treatment plants. At abandoned mine sites with acid mine drainage mine or neutral mine drainage, Zn concentrations typically remain elevated and persist into downstream environments. We present a compilation of Zn geochemical data collected at acid and neutral mine drainage sites from bituminous coal and epithermal gold mine drainages from both active and abandoned mines. Geochemical modelling using Phreeqc indicates that secondary Zn minerals are unlikely to influence the concentration of Zn except in rare circumstances where Zn concentrations are high (>100 mg/L) and mine drainage pH>7. Adsorption modelling using WHAM indicates that Zn concentrations are unlikely to be attenuated by adsorption onto Fe and Al precipitates that could form during neutralisation or oxidation of mine drainages except where the ratio of precipitate to dissolved Zn is high. Therefore the Zn concentration in mine drainages where active treatment is not completed is primarily controlled by the abundance of source minerals, the rate of dissolution of these minerals and dilution.

Keywords: Zinc, acid mine drainage (AMD) neutral mine drainage (NMD), adsorption, solubility.

Introduction

Zinc concentrations have been measured in mine drainages from many mine environments in New Zealand and in rock leachate experiments for mine drainage prediction studies (Black and Craw, 2001; Giles et al., 2010; McCauley et al., 2010b; Pope et al., 2010a and others). Zinc is always one of the most abundant transition metals present in mine drainage seeps or leachates from bituminous coal mines and from epithermal metal mines. Sulphide minerals are the main source of Zn in mine drainages, sphalerite (ZnS) at epithermal metal mines (Christie and Brathwaite, 2006) or from Zn impurities in pyrite (FeS₂) at coal mines (Pope et al., 2010b; Weber et al., 2006; Weisener and Weber, 2010). Zn from other minerals (such as muscovite) during AMD formation is also possible and concentrations of Zn in whole rock analysis are similar to concentrations in sulphide minerals for sub-bituminous coal measures in southern New Zealand (Black and Craw, 2001). At operating mine sites Zn is removed from mine drainage discharges by active chemical water treatment plants. However, at abandoned mines, discharges of Zn into the wider surface water environment at concentrations that exceed background concentrations and environmental protection guideline values can occur.

We present a compilation of data on Zn concentrations in New Zealand mine drainage environments and rock leachate experiments from literature review, company presentations and from company datasets. Our modelling indicates minerals that might limit the concentration of Zn through precipitation after release into mine drainages such as Zn-hydroxides, -oxides, -sulphates, or -carbonates, are soluble under conditions found in most mine drainage aqueous environments. Adsorption of Zn onto mineral surfaces occurs mostly between pH 6 and 8 (depending on ratio of sorbent to sorbate) (Dzombak and Morel, 1990). Therefore, at abandoned mine sites, elevated concentrations of Zn are likely to be partitioned

into aqueous species rather than minerals or adsorbed species within and downstream of mine discharges, especially in acidic mine drainages ($\text{pH} < 6$). We interpret data from these highly variable chemical environments with geochemical modelling and consider the implications for remediation of historic mine sites and future development of mineral resources in New Zealand.

Methods

Mine drainage geochemistry

Analyses to support this study were collected from literature and from previous studies conducted by the authors. Details related to sample sites and geochemical analyses are published elsewhere (Miller, 1987; Pope et al., 2010a; Pope et al., 2011; Pope and Weber, 2013; Pope et al., 2010b). Mine drainage samples collected during this study were mostly collected as close to the source of the mine drainage seep as possible. Column leach test samples were collected using standard methods (Smart et al., 2002). Mine drainage titrations were completed using 0.05 g additions of CaCO_3 to 1L AMD with 20 mL subsamples removed for analysis. All analyses of these samples were completed by commercial laboratories. Where total aqueous concentrations are reported samples were collected and acidified ($\text{pH} < 2$). Where dissolved aqueous concentrations are reported were filtered to $0.45 \mu\text{m}$ using a disposable syringe and filter, then preserved in acid ($\text{pH} < 2$). Both total and dissolved concentrations of Zn and other components were measured by ICP-MS or ICP-OES. Supporting pH measurements were made using a field calibrated YSI multi probe, alkalinity was measured by titration.

Modelling

Aqueous speciation and mineral saturation modelling was completed using PhreeqC (Parkhurst and Appelo, 1999). The saturation modelling reflects controls on Zn concentration at the time of discharge into the wider environment because samples are from the source of mine drainage seeps rather than downstream of mines. Samples collected downstream of mines have been avoided because site specific factors such as mixing with other surface water would make interpretation difficult. In addition, treatment systems usually function most efficiently with minimal dilution and therefore seep samples are most relevant to treatment studies. All modelling was completed with a representative suite of major cation and anion chemistry so that ionic strengths and precipitation of other secondary minerals is incorporated into the modelling.

Partitioning between dissolved ionic species and adsorbed species was completed using WHAM (Tipping, 1994; Tipping et al., 2002). The approach to adsorption modelling was to assume the Fe and Al concentrations dissolved in acidic or reduced mine drainages would precipitate and provide a substrate for adsorption. The sorbate to sorbent mass ratios for modelling were calculated from the measured dissolved Zn concentrations and measured total Fe and Al concentrations assuming conversion of Fe to $\text{Fe}(\text{OH})_3$ and Al to $\text{Al}(\text{OH})_3$. This means that the adsorption modelling reflects changes in dissolved to adsorbed Zn concentrations that can be achieved through neutralisation by hydroxide to pH 8 or oxidation of mine drainages without addition of other chemical reagents to increase adsorption.

Results

Bituminous coal AMD and column leach analyses

The pH was commonly between 2 and 4 in AMD from New Zealand's bituminous coal mines. Zn was typically one of the three most abundant dissolved transition metals, along with Fe and Mn, and the Al was also usually elevated. At the seeps, the Zn concentration was between 0.1 and 18 mg/L (Davies 2009; Davies et al., 2011b; Mackenzie 2010; Mackenzie et al., 2011; Pope et al., 2010a; McCauley et al., 2010). The concentration of Fe and Al was typically between 1 and 100 mg/L (Table 1). Where data was available from filtered and unfiltered samples, the Zn was commonly close to 100% dissolved in seep samples.

Table 1. Range of concentrations of Zn, Fe and Al in NZ mine drainages.

Acid Coal Mine Drainages	pH		Alkalinity mg CaCO ₃ /L		Fe mg/L		Al mg/L		Zn mg/L	
	max	min	max	min	max	min	max	min	max	min
Pope et al, 2010	5.85	2.53	<	<	105	0.86	115	0.6	4.08	0.006
McCauley et al, 2010	3.7	2.05	<	<	1300	0.03	600	3.1	18	0.08
Davies et al, 2011	4.3	2.6	<	<	60	32	66	39	1.89	1.02
Mackenzie 2010	3.96	2.94	<	<	3.3	0.97	55	1.1	3	0.15
Column Leach										
Pope et al, 2011, 2013	4.5	1.8	<	<	10200	0.2	1190	2.2	99	0.4
Neutral Coal Mine Drainages										
	7.31	5.86	940	120	13	0.068	0.2	<	0.17	0.0037
Column Leach										
	8.3	4.1	75	1	0.16	0.02	0.08	0.019	1.3	0.001
Epithermal Metal Mine Drainages										
Peterson & Kindley, 1993	7	5	nd	nd	10	1	nd	nd	4	1
Cameron, 1991	7	6	nd	nd	0.2	10	nd	nd	5	0.5
Pang, 1995	7.8	6.6	nd	nd	9.75	3.97	nd	nd	25	15.5
Giles et al, 2010	7.6	2.9	75	0	8.6	0.04	nd	nd	173	0.03
Column leach										
Miller, 1987	6.4	7.8	nd	nd	1100	0.2	595	<	11.9	0.05

Bituminous coal NMD and column leach analyses

In neutral mine drainage from coal mines, Zn was also commonly one of the three most abundant transition metals present; however, the Zn concentrations were lower than in the acid coal mine drainages, with a maximum of 170 µg/L (Table 1). Iron concentrations were variable, up to 12 mg/L, and reflected the presence of dissolved Fe(II). Typically the NMD contained alkalinity so oxygenation caused Fe(II) oxidation and precipitation of Fe(OH)₃ or similar minerals and these minerals provide a substrate for adsorption of Zn. The column leach data (Table 1) had a low range of concentrations for dissolved Fe (maximum 116 µg/L) and occasionally relatively high concentrations of Zn (>1 mg/L). Zn was often the most abundant metal present in these leachates, with the exception of alkali and alkaline earth metals.

Epithermal metal mine drainage and column leach analyses

In mine drainage from abandoned epithermal metal mines or upstream of water treatment at active mine sites, Zn was commonly one of the most abundant trace metals (along with Fe, Mn, and Cu), with concentrations usually between 0.1 and 20 mg/L (Table 1; Cameron 1991; Giles et al., 2010; Peterson and Kindley, 1993). Occasionally, higher Zn concentrations were measured in mine drainage seeps, up to 179 mg/L (Giles et al., 2010), and up to 563 mg/L in tailings-impacted groundwater (Pang, 1995).

In these mine drainages, Fe was commonly present at relatively low concentrations, 0.4 to 10 mg/L, similar to NMD from coal mines. Leachate experiments indicate that Fe can be present at high concentrations (1100 mg/L) under acidic conditions. Leachate from epithermal mineral deposits have a lag period of neutral mine drainage before acid formation occurs, because carbonate minerals neutralise acid produced by sulphide mineral oxidation (Craw and Chappell, 1998; Miller, 1987).

Discussion

Zn mineral saturation

All New Zealand are undersaturated with respect to Zn minerals that could precipitate in these environments (Fig. 1) except in rare neutral mine drainages from epithermal deposits (Fig. 2). In neutral coal mine drainages Zn mineral saturation is not reached. In acidic coal mine drainages, neutralisation to about pH 6 using limestone is achievable through fine limestone dosing (Davies et al., 2011a) or to between 4 and 7 using limestone-based passive treatment systems (Mackenzie, 2010; Mackenzie et al., 2011; Trumm and Watts, 2010; Trumm et al., 2008). However, high pH (>6) is only achieved at extended residence times. These conditions are unlikely to lead to Zn mineral precipitation from coal mine drainage (Fig. 1).

Minerals that can be saturated in neutral epithermal deposits include carbonate minerals (smithsonite, ZnCO_3 and $\text{ZnCO}_3 \cdot 2\text{H}_2\text{O}$), and hydroxide minerals (Zn(OH)_2), and hydroxi-sulphate ($\text{Zn}_4(\text{OH})_6\text{SO}_4$) minerals (Fig. 2). This means that the high Zn concentration in these mine drainages could be controlled by secondary minerals that precipitate as sphalerite breaks down.

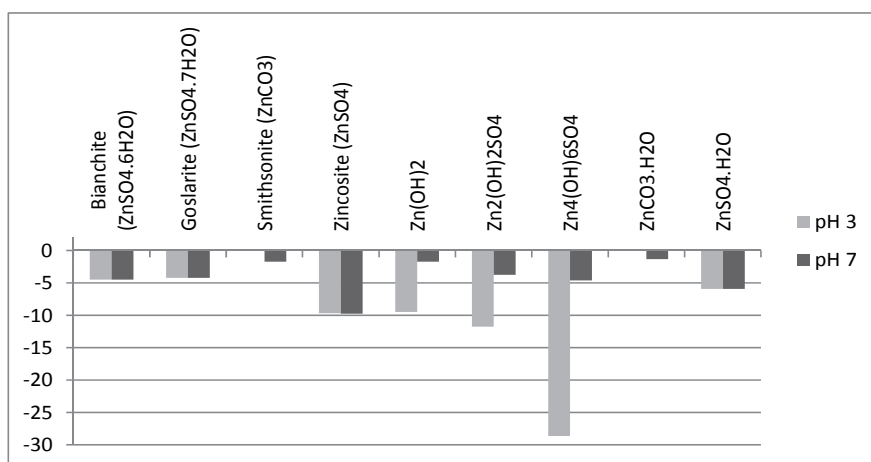


Figure 1. Zn mineral saturation in coal mine drainage and neutralised AMD from coal mines.

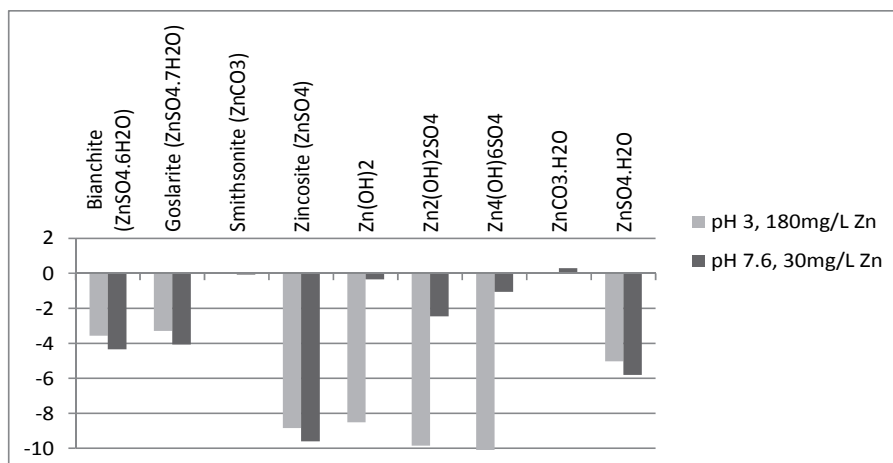


Figure 2. Zn mineral saturation in AMD from epithermal deposits.

Zn adsorption

Adsorption of trace elements onto poorly crystalline Fe and Al minerals is controlled by pH and is influenced by ionic strength, aqueous speciation, and competition for adsorption sites (Dzombak and Morel, 1990; Smith, 1999). The effectiveness of adsorption for Zn removal from mine drainage during neutralisation also depends on the ratio of sorbent (Fe and Al minerals) to sorbate (dissolved Zn). Using the range of concentrations reported for major cations (Fe, Al, and Zn) and anions for coal AMD, modelling with WHAM can be used to indicate the amount of Zn that can be adsorbed onto precipitates that form in these environments either through oxygenation and oxidation or through neutralisation.

During neutralisation of AMD, a variety of Fe and Al oxide, hydroxide, and hydroxyl-sulphate minerals form (Nordstrom and Alpers, 1999). In New Zealand coal mine drainages, the Fe minerals are most likely to be schwertmannite ($\text{Fe}_8\text{O}_8(\text{SO}_4)\text{OH}_6$) and ferrihydrite ($\text{Fe}(\text{OH})_3$), and the Al minerals are most likely to be basaluminite and boehmite (AlOOH) (Davies et al., 2011a; Pope and Trumm, 2014). These minerals form suitable substrates for adsorption of Zn.

At the concentrations of Zn, Fe and Al present in coal AMD then neutralisation of to pH ~7 is required to adsorb a high (60-100) percentage of Zn (Fig. 3). Adsorption of 20-40% of Zn occurs at about pH 6. This means that limestone based neutralisation will of coal AMD not reliably produce a pH that will encourage adsorption of Zn onto the substrate that forms. Limestone based neutralisation typically achieves pH 6 and pH 7 is only achieved at high residence times or will extended mixing periods.

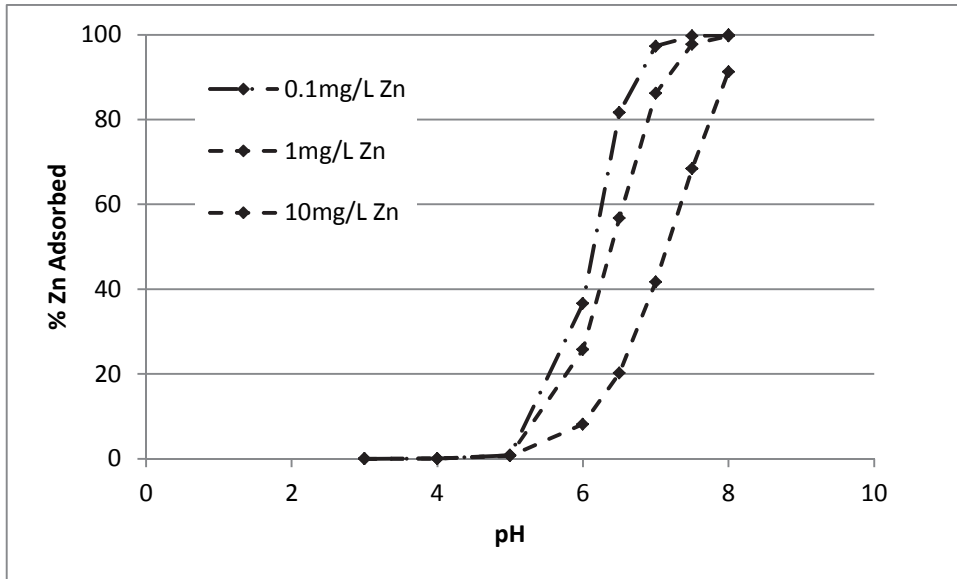


Figure 3. Adsorption of Zn onto Fe and Al minerals that could precipitate from coal AMD (~50 mg/L Fe & Al during neutralisation).

In NMD that contain dissolved Fe(II), oxygenation will cause oxidation to Fe(III) and precipitation of Fe(OH)₃. The effectiveness of this substrate to adsorb Zn in the mine drainage and column leach experiments depends on the pH and abundance of Fe (Fig. 4). At pH > 7.5 and with a ratio of 10 mg/L Fe to 0.01 mg/L Zn modelling indicates that over 90% of Zn will be adsorbed. However, under the other scenarios modelled, less Zn can be adsorbed.

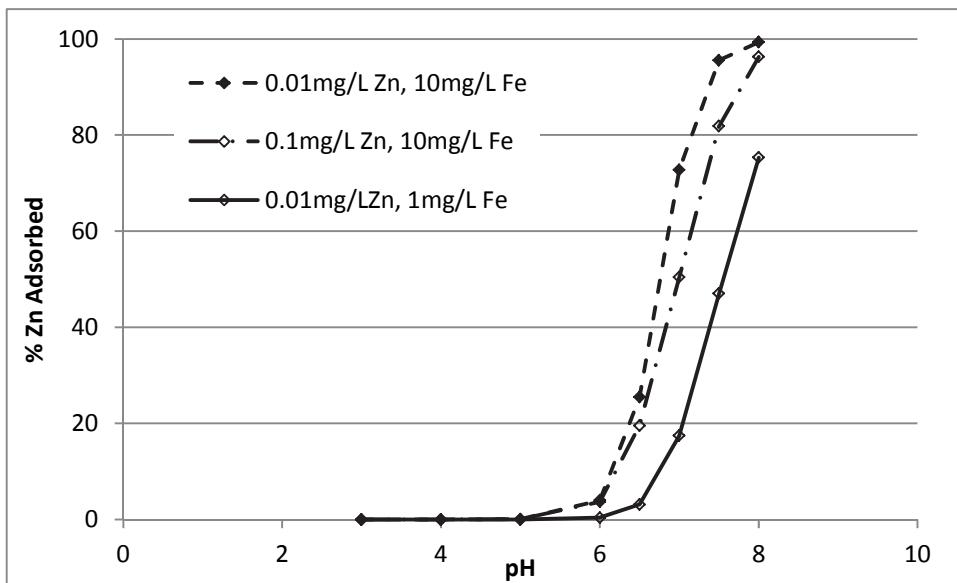


Figure 4. Adsorption of Zn onto Fe minerals that could precipitate from coal NMD.

Most reported analyses for epithermal mine drainages have circum-neutral pH and relatively low concentrations of Fe. Therefore, Zn adsorption during precipitation of secondary Fe(III) minerals is unlikely to significantly decrease the dissolved Zn (Fig. 5).

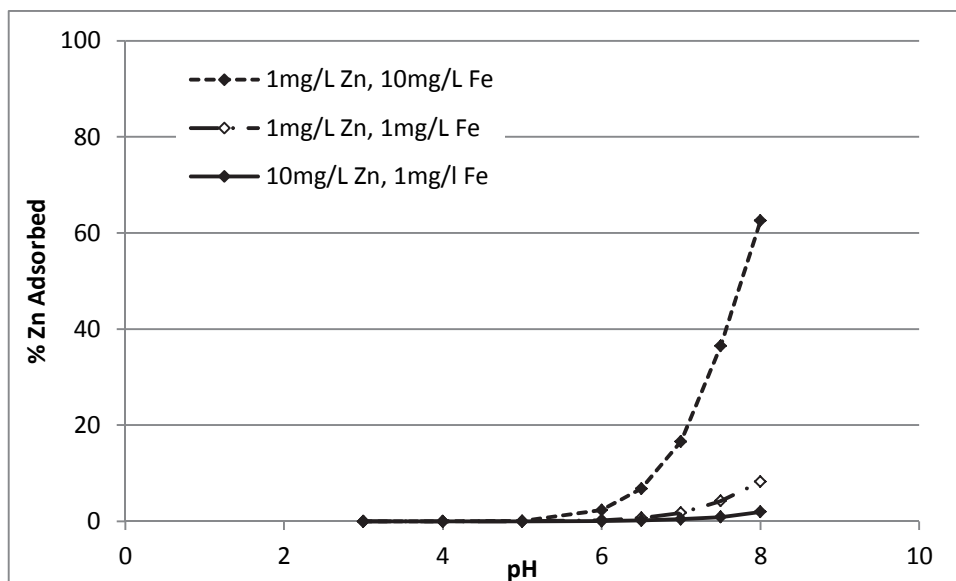


Figure 5. Adsorption of Zn onto Fe minerals that could precipitate from epithermal deposit AMD.

Guideline values for Zn concentrations in water

Concentrations of Zn in most freshwater usually does not naturally exceed 0.01 mg/L (ANZECC, 2000); however, its concentration in mine drainages almost always exceeds this value, commonly by 1-2 orders of magnitude, and by up to more than four orders of magnitude at epithermal metal mine sites. Guideline values (Table 2) for water use (drinking, irrigation, etc.) range between 1.5 and 20 mg/L because Zn is an essential micro-nutrient for plants and animals, and has minimal toxic effect (ANZECC, 2000; MOH, 2005) for these organisms. However, guideline values for protection of aquatic ecosystems are much lower, between 2.4 and 31 $\mu\text{g/L}$, with scope to adjust these values depending on site-specific water chemistry, because some aquatic organisms are sensitive to elevated Zn concentrations.

Table 2. Range of concentrations of Zn, Fe and Al in NZ mine drainages.

Guideline	ANZECC 2000 99% protection of aquatic ecosystems	ANZECC 2000 80% protection of aquatic ecosystems	ANZECC 2000 Irrigation water	ANZECC 2000 Livestock drinking water	MOH 2005 Drinking water
Zn	2.4 $\mu\text{g/L}$	31 $\mu\text{g/L}$	2-5 mg/L	20mg/L	1.5mg/L

Guideline values for Zn in water span almost five orders of magnitude, which complicates decision making for discharging Zn to the environment. For example, leakage of livestock drinking water with 20 mg/L could significantly exceed values desired for surrounding or downstream freshwater environments. The concentration of Zn produced by mineral resource developments in areas where agriculture occurs is unlikely to cause concern. However, the Zn concentration in mine drainages will require planning, management, and likely active treatment in resource developments within areas that have pristine water quality. It is possible that acceptable protection of the ecosystem can be achieved with discharges that exceed the current guideline values; however, this would require site-specific ecological toxicity testing.

Summary and Conclusion

Elevated Zn concentrations in AMD with a $\text{pH} < 5$ are not controlled by mineral precipitation reactions or attenuated by adsorption onto minerals that precipitate during mine drainage evolution. Therefore, the concentration of Zn will accumulate in AMD at $\text{pH} < 5$ and will be controlled by the abundance and dissolution rate of Zn bearing minerals. In the downstream environment, dilution is likely to be the most important factor unless there is an abundant substrate for adsorption. Water recycling or reuse is likely to increase Zn concentrations in mine impacted water, and saturation with respect to Zn minerals will only occur at high concentrations ($> 100 \text{ mg/L}$).

Zn concentrations in NMD with $\text{pH} > 6$ (based on modelling) could be attenuated by adsorption onto Fe and Al mineral precipitates. However, this attenuation is only likely to be significant where Zn concentrations are relatively low ($< 1 \text{ mg/L}$) and the amount of adsorbing minerals is relatively high ($> 10 \text{ mg/L}$). The only mine drainages in this study that typically have concentrations of Fe and Al that could form precipitates with concentrations $> 10 \text{ mg/L}$ are coal AMD. These will always require neutralisation in order to precipitate the Fe and Al minerals, and if the neutralisation is completed with limestone, reactions become slow at $\text{pH} > 6$, and so complete adsorption, which requires a $\text{pH} > 7$, is unlikely to occur.

In NMD (epithermal or coal), dissolved Fe(II) can be present that will form Fe-hydroxide precipitates on oxidation. However the Fe concentration is generally low ($< 10 \text{ mg/L}$), and therefore adsorption will only be significant if Zn concentrations are also low ($< 0.1 \text{ mg/L}$). This is unlikely at epithermal metal deposits where Zn concentrations are typically $> 1 \text{ mg/L}$.

The conservative behaviour of Zn means that limestone-based neutralisation of AMD is unlikely to reliably treat Zn, and alternative strategies must be adopted. Alternative strategies include either active treatment, where sorbent phases are added and pH is increased to promote effective adsorption, or passive treatment by systems that promote sulphate reduction and precipitation of Zn-sulphide phases, or trapping of Zn within other sulphide minerals. Sulphate-reducing passive treatment systems to treat trace element-rich AMD from coal mines in New Zealand have been studied (McCauley et al., 2009; Trumm et al., 2008; Uster et al., 2014), with successful Zn removal. Oxidising passive treatment systems that cause $\text{pH} > 7$ through use of CaO-bearing waste materials (steel slag or cement kiln dust) could also effectively remove Zn.

Downstream processes that might attenuate Zn in otherwise untreated mine drainage discharges will be site specific and are limited to dilution and adsorption. Adsorption substrates can be more abundant in the wider environment, depending on the surrounding geology and geochemistry, and include Fe and Al oxy-hydroxide, clays, and organic particles. The guideline values for Zn discharging into aquatic ecosystems are low ($2.4\text{--}31 \text{ }\mu\text{g/L}$), while guidelines for use of water containing Zn are high ($1\text{--}20 \text{ mg/L}$). In general, this means that consenting for either coal or epithermal gold mines will require careful planning for Zn, either with an active treatment system, an accepted risk to ecology, or possibly discharge of mine water to irrigation storage or the town water supply (assuming that the water does not have elevated concentrations of other regulated components).

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